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(54) **Oxygen-complexing ultrathin films by interfacial polymerization.**

(57) Interfacially-polymerized ultrathin films containing oxygen-complexing functional groups are disclosed, both with and without supports. Various applications are disclosed, including selective membranes and sorbents.

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OXYGEN-COMPLEXING ULTRATHIN FILMS BY INTERFACIAL POLYMERIZATION

BACKGROUND OF THE INVENTION

Over the past three decades, considerable emphasis has been placed on the development of very thin
 5 polymeric films. For the most part, these thin films have been used as membranes, to effect chemical
 separations. Such processes as reverse osmosis for water desalination, gas separations as used in the
 purification of natural gas and in the production of oxygen-enriched air, and pervaporation which is used to
 break commercially important azeotropes, all rely on the availability of very thin, highly selective mem-
 10 branes. These and other processes are described in Volume VII of the "Techniques of Chemistry" series
 entitled "Membranes in Separations" (1975) by Hwang and Kammermeyer. In all membrane separation
 processes, the transmembrane flux is a key criterion in determining the cost of the process. High flux is
 generally associated with thin membranes, in keeping with Fick's first law, and considerable research and
 development has been expended toward making very thin, yet still highly selective membranes.
 "Selectivity" refers to the ability of the membrane to pass one species in a mixture while retaining other
 15 species. High selectivity is essential to effecting clean separations. The first technical breakthrough was the
 reverse osmosis membrane invented by Loeb and Sourirajan and disclosed in U.S. Patent No. 3,133,132.
 Numerous types of membranes have been made since then using the Loeb-Sourirajan technique. See, for
 example, Kesting, 50 Pure & Appl. Chem. 633 (1978), who discloses asymmetric (skinned) cellulosic
 membranes, and Broens et al., 32 Desalination 33 (1980), who disclose similar membranes of cellulose
 20 acetate, polysulfone, polyacrylonitrile, and polydimethylphenyleneoxide.

The second breakthrough in making thin, selective membranes was due primarily to Cadotte. Cadotte
 borrowed from the teachings of Morgan, who first described in detail "interfacial polymerization." Interfacial
 polymerization (IP) is a process in which a very thin film (or membrane) can be made by reacting two
 25 monomers at the interface between two immiscible solutions. It is best described by example. "Nylons" are
 a class of polymers referred to as polyamides. They are made, for example, by reacting a diacid chloride,
 such as adipoyl chloride, with a diamine, such as hexamethylene diamine. That reaction can be carried out
 homogeneously in a solution to produce the polymer in resin form. However, it can also be carried out at an
 interface by dissolving the diamine in water and floating a hexane solution of the diacid chloride on top of
 the water phase. The diamine reacts with the diacid chloride at the interface between these two immiscible
 30 solvents, forming a polyamide film at the interface which is rather impermeable to the reactants. Thus, once
 the film forms, the reaction slows down drastically, so that the film remains very thin. In fact, if the film is
 removed from the interface by mechanical means, fresh film forms at the interface, because the reactants
 are so highly reactive with one another.

Cadotte used such knowledge of interfacial polymerization techniques to produce extremely thin,
 35 supported films such as are disclosed in U.S. Patent No. 4,277,344. As a modification of the two immiscible
 liquid phases, he dissolved one reactant in a solvent and then used that solution to fill the pores of a
 microporous substrate membrane. He then exposed that wet membrane to a second, immiscible solvent
 containing the other reactant. An interfacially polymerized, very thin film formed at the surface of the
 microporous substrate, which then served as a support for the very thin film. Numerous adaptations of the
 40 Cadotte technology have been made using essentially the same IP method.

Morgan, in Volume 20 of the "Polymer Reviews" series entitled "Condensation Polymers: By Interfacial
 and Solution Methods" (1965), describes numerous chemistries that can be used to make polymers
 interfacially. Among the important chemistries are: polyamides, as already described; polyureas,
 polyurethanes, polysulfonamides, and polyesters; several other less important classes are also described.
 45 Morgan and others have also described the factors important to making continuous, thin interfacial films:
 temperature, the nature of the solvents and co-solvents, the concentrations of the two reactants, and the
 reactivity of the two monomers. *Id.* at pages 486-509. Refinements of the art developed over the past 20
 years include the use of "blocked" or protected monomers that can be later unblocked to alter the
 chemistry of the finished film, the use of posttreatment of the films to alter their chemistry, and the use of
 50 heteroatoms in the monomers to alter the properties of the final film or membrane. In the classical organic
 chemistry sense, these alterations would be referred to as changes in the chemical "functionality," i.e.,
 changes in those groupings of atoms that cause a substance to enter into its characteristic chemical
 reactions with another substance.

SUMMARY OF THE INVENTION

According to the present invention there is provided a class of thin films with a different kind of "functionality" than the classic organic chemistry "functionality" referred to above. In the context of the present invention, "functionality" is defined to mean the state of being physicochemically reactive, such as in the case of a moiety that has oxygen-specific reversibly-complexing complexing sites. The term is not intended to include characteristic chemical reactivity owing to the presence of free "functional" groups in the classic organic chemistry sense, such as a vinyl group, a hydroxyl group or a carboxyl group. The thin films of the present invention are physicochemically functional in the sense of containing moieties capable of oxygen complexation. It has been found that the IP method can be used to produce ultrathin (20 to 2000 nanometers thick) films that contain such functionality as an integral part of the polymeric film, such that the ultimate film retains the physicochemical functionality of the original monomeric moiety. The IP method of the present invention provides means for incorporation of the oxygen-complexing monomeric moiety into the polymeric film without substantially altering its oxygen-complexing functionality, thus endowing the film with that same oxygen-complexing functionality. Thus, in a sense, the present invention may be regarded as a method of binding an oxygen-complexing moiety within a thin polymeric matrix, while at the same time leaving that moiety available to enter into its characteristic oxygen-complexing reactions.

Preparation of such ultrathin reversibly oxygen-complexing films is essentially a two-step process comprising the steps of:

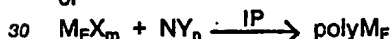
(1) forming one or more polymerizable derivatives of a discrete monomeric or prepolymeric molecule possessing oxygen-complexing functionality; and

(2) forming by IP an ultrathin film of the derivative(s) of the molecule so as to imbue the film with substantially the same oxygen-complexing functionality as possessed by the original monomeric or prepolymeric molecule.

In terms of a chemical reaction, the following representational scheme summarizes the method of the present invention:



or



where M_F is a monomeric or prepolymeric molecule or moiety with an oxygen-specific complexing functionality; N is a monomeric or prepolymeric molecule or moiety not having any oxygen-specific complexing functionality; X and Y are chemically functional groups in the classic organic chemistry sense, such as amines and acid chlorides, which have complementary reactivity (such as in a condensation reaction) allowing them to undergo IP; m and n are integers ≥ 2 ; IP is an interfacial polymerization reaction; and $\text{poly} M_F$ is an interfacially-polymerized polymer containing discrete repeating units of the oxygen-complexing moiety M_F .

The conversion of the original oxygen-complexing monomer, M_F , into the polymerizable monomeric derivatives, $M_F X_m$ or $M_F Y_n$, is carried out by standard synthetic techniques so as to retain the oxygen-complexing functionality of M_F . The required synthetic techniques will necessarily be different for the various types of X and Y reactive groups which could be used and may also have to be modified to assure that the oxygen-complexing functionality of M_F is retained. Specific examples of the X and Y mutually reactive groups include amines and acid halides (to form polyamides), alcohols and acid halides (to form polyesters), thiols and acid halides (to form polythioesters), amines and isocyanates (to form polyureas), alcohols and isocyanates (to form polyurethanes), and amines and sulfonyl halides (to form polysulfonamides). Other lesser known but potentially useful examples of mutually reactive groups capable of entering into condensation reactions are set forth in Chapter 9 of Morgan, "Condensation Polymers: By Interfacial and Solution Methods" (1965).

DETAILED DESCRIPTION OF THE INVENTION

According to the present invention, ultrathin films containing reversibly oxygen-complexing functionality may be prepared by IP methods. The term "films" is meant to include films in the shape of flat sheets, tubes, hollow fibers, microcapsules, or beads. In most applications, because the thin films are physically too weak to be self-supporting, in use they would be applied as a coating on some physically robust substrate in one of the above-described shapes.

The method of interfacial polymerization of oxygen-complexing molecules can also be applied to the preparation of highly selective, high flux membranes and of sorbents for oxygen separations. To be commercially useful, membranes must combine high selectivity, i.e., they must transport the oxygen species to the exclusion of others, with high flux. Membranes made according to the present invention offer this combination. The basic steps in fabrication of such selective membranes and sorbents are: (1) select a chemical moiety that is reversibly-complexing with oxygen; (2) derivatize that moiety into two complementary derivatives such that an IP reaction can be carried out between them; and (3) make an ultrathin membrane by IP on a suitable microporous substrate. The membrane will have the selectivity inherent in the original oxygen-selective chemical moiety, and the membrane will exhibit very high flux because of its great thinness. If the membrane is made under conditions that lead to a crosslinked polymeric matrix, for example, by reacting a trifunctional-derivatized moiety with a complementary difunctional-derivatized moiety, the resulting membrane should also exhibit good stability.

In the event that it is desired to produce a selective oxygen sorbent composition, the IP reaction may be merely carried out at the interface of two immiscible solvents without a microporous support. Such sorbent film may be used in a manner similar to the way in which a molecular sieve or a carbon sorbent is used, i.e., the film in granular form or on the surface of a support may be exposed to the fluid from which oxygen is desired to be removed. Oxygen is then stripped from the sieve or sorbent in a relatively pure form by the use of a lower pressure or a higher temperature.

Such oxygen-complexing films comprise a thin polymeric network of reversibly reactive sites. The reversibly reactive sites can reversibly complex with oxygen that is in turn transported through the film by a driving force such as a concentration gradient or a pressure differential.

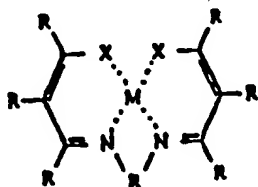
Broadly, such oxygen-selective membranes are thin film composite membranes comprising a microporous support and the thin film interfacial polymerization reaction product of M_FX_m and NY_n , wherein M_F is a moiety having oxygen-specific reversibly-complexing complexing sites, N is a moiety not having any oxygen-specific complexing sites, X and Y are groups that are mutually reactive in a condensation reaction, and m and n are integers ≥ 2 . The X and Y groups that are mutually reactive in a condensation reaction are selected from any of the mutually reactive groups mentioned in "Background of the Invention" above, and are preferably selected from acid halides, amines, alcohols, aldehydes, thiols, isocyanates and sulfonyl halides.

It is known that certain metalloporphyrins, certain metallo-Schiff base complexes, and certain metallophthalocyanines can selectively complex oxygen and that membranes containing these groups can selectively transport oxygen. See U.S. Patents Nos. 4,451,270 and 4,542,010. In connection with the selective transport of oxygen over nitrogen see Hishide et al. in Macromolecules, Vol. 20, pp. 417-422 (1987), who describe such selective oxygen transport in a polymeric membrane containing Co(II) porphyrin groups. It is also known that certain metalloporphyrins such as cobalt(II) or iron(II) tetraphenyl porphyrin can selectively bind carbon monoxide. See Chang et al., 72 Proc. Natl. Acad. Sci. USA, 1166 (1975).

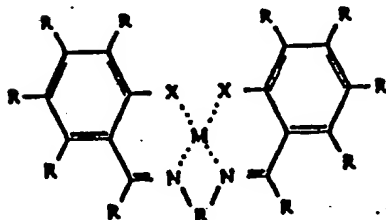
Such metallocomplexes may be incorporated into ultrathin films by the IP methods described herein. The metallo-Schiff bases are described in detail in commonly assigned U.S. Patent Nos. 4,451,270 and 4,542,010, the descriptions of which are incorporated herein by reference, while the metalloporphyrins and metallophthalocyanines are described in detail in commonly assigned U.S. Patent No. 4,784,736, the description of which is also incorporated herein by reference. The general structures of these metallocomplexes are shown below

Metallo-Schiff Bases

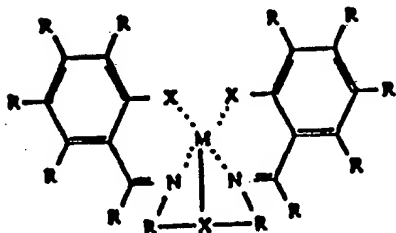
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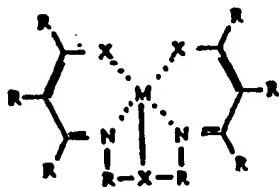


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wherein M is a metal of +2 valence selected from cobalt, iron, copper, nickel, manganese, ruthenium and rhodium; X is -O-, -S-, -P- or -N-;

R is hydrogen, alkyl, alkylene, aryl, arylene, halogen, alkoxy or a nitrogen-containing moiety; R' is hydrogen, alkyl, aryl, pyridinyl, R'', alkyl-R'', or aryl-R''; R'' is hydrogen, Hal, NH₂, CH₂NH₂, SH, OH, COHal, COOH, NCO, or SO₂Hal; and Hal is a halide.

An exemplary method of preparing a metalloporphyrin and incorporating its oxygen-complexing physicochemical functionality into an interfacially polymerized membrane follows.

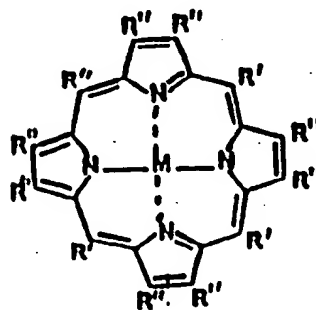
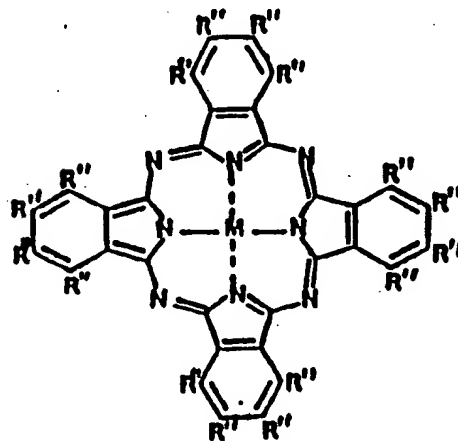
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Example 1

The tetracarboxylic acid derivative of tetraphenylporphyrin, 5,10,15,20-tetra(p-carboxyphenyl) porphyrin was converted to its acid chloride derivative by refluxing 1 gram of the porphyrin in 50 ml of thionyl chloride for 18 hours. Excess thionyl chloride was removed by vacuum distillation until the solid residue appeared to be dry. A vacuum of 1 torr was applied at 50° C for 20 minutes to remove the last traces of thionyl chloride and HCl produced by the reaction. The conversion of carboxylic acid groups to acid chloride groups was inferred from the subsequent characteristic reactivity of the product with amines to form a polymer. This acid chloride derivative of the tetraphenylporphyrin was interfacially polymerized with diethylenetriamin (DET) on a microporous support by a three-step process.

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First, a microporous polypropylene support comprising a film about 25 microns thick was clamped between two 2.5-inch-ID polypropylene annular rings. This assembly was then placed in a petri dish that

MetalloporphyrinsMetallophthalocyanines

contained a 10^{-3}M solution of the acid chloride-derivatized tetraphenyl porphyrin monomer in chloroform. The level of the porphyrin solution was adjusted so that it coincided with the upper surface of the microporous support. Second, the reservoir formed by the upper ring was filled with a 10^{-3}M aqueous solution of DET. The interfacial polymerization reaction then proceeded at the chloroform-water interface.

5 Finally, the reaction was stopped after 30 minutes by removing the upper aqueous layer, leaving the polyporphyrin film on top of the microporous support. Prior to characterizing the film, the upper and lower surfaces of the microporous support were washed alternately with chloroform and water to remove any of the unreacted monomers.

10 The resulting polyporphyrin film was converted to the cobalt(II) porphyrin form by placing the film in a solution of 0.1 g cobalt(II) chloride in 100 ml dimethylsulfoxide at 80°C for 16 hours. Conversion of the free base porphyrin polymer to the cobalt(II) porphyrin polymer was evidenced by the disappearance of the four Q bands characteristic of the metal-free porphyrin, and by the appearance of the alpha and beta bands characteristic of the metal-containing porphyrin, in the region of the UV/visible spectrum between 400 and 700 nm.

15 The reversible oxygen-sorbing property of the cobalt(II) porphyrin polymer was demonstrated by the following experiment. The cobalt/porphyrin polymer film was placed in a DMSO solution containing a large excess of the axial base dimethylaminopyridine (DMAP) (the molar ratio of DMAP to porphyrin was about 2000). An "axial base" donates electrons to the coordinated metal, thereby improving the reversible oxygen-binding capacity of the metallo-porphyrin. After two hours, the cobalt/porphyrin polymer film was removed from the DMSO solution, rinsed in chloroform, and then air dried. The cobalt/porphyrin polymer film was then placed in a gas-tight cell equipped with an inlet and outlet port so that the cell could be purged and pressurized with a gas. The polymer film was then exposed to 75 psia of oxygen at room temperature. The Soret band, originally at 418 nm, shifted to 444 nm. This peak shift, characteristic of the formation of an oxygen complex (see Bengelsdijk et al., 97 JACS 22 (1975) and Nishide et al., 19 Polm. J. 7 (1987)), occurred within seconds after exposure to the oxygen. After three minutes the oxygen was flushed from the cell with nitrogen. The spectrum reverted to its original pattern within one minute. The film was cycled between oxygen-loaded and oxygen-unloaded states several times. The oxygen-loaded polymer film always exhibited the Soret band at 444 nm while the oxygen-unloaded polymer film always showed the Soret band at 418 nm, indicating the film reversibly sorbed and desorbed oxygen.

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Example 2

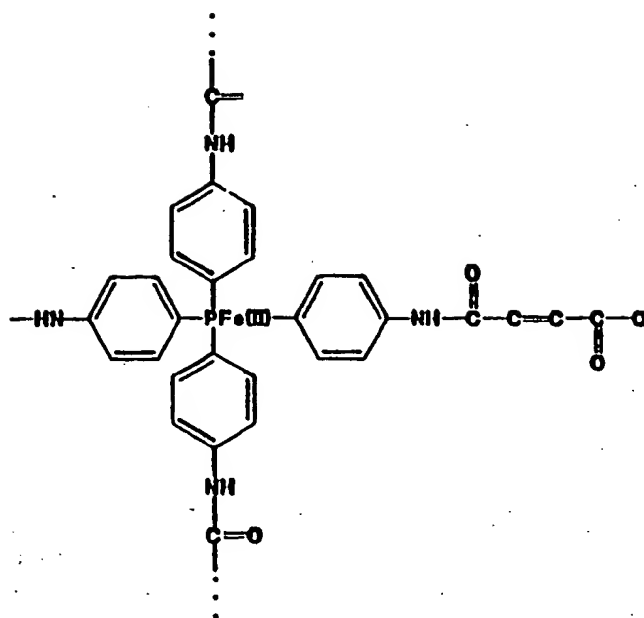
35 A solution of a metallo-porphyrin such as tetra(aminophenyl)-porphyrin iron(II) in water or dimethylsulfoxide (DMSO) or other suitable solvent is held within the pores of a microporous polymeric support membrane and then exposed to a solution of an acid halide such as fumaryl chloride in a hydrocarbon solvent such as hexane to form an ultrathin polymeric membrane on the surface of the support containing recurring units of structure XIV

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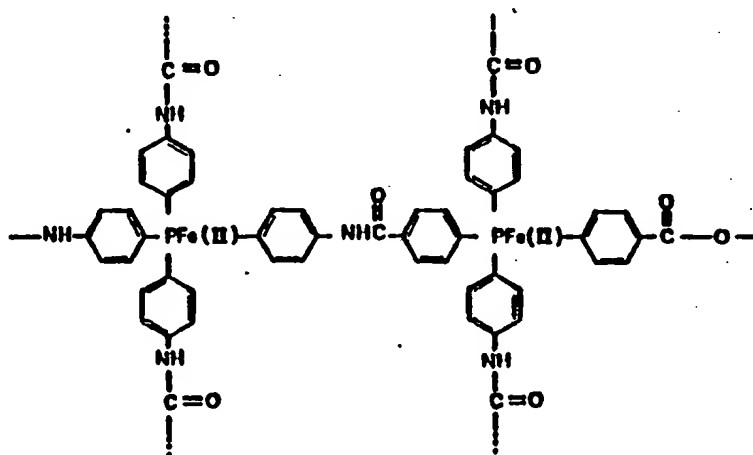


XIV

where PFe(II) is iron (II) porphyrin.

Example 3

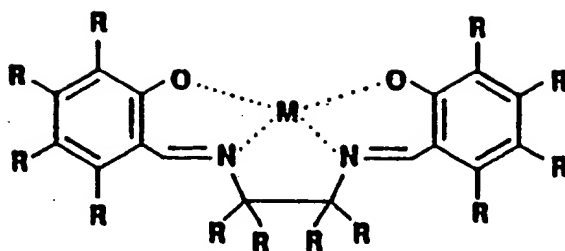
An aqueous solution of tetra-(aminophenyl)porphyrin iron(II) is reacted with a solution of an iron(II) porphyrin acid halide such as tetra-(carboxyphenyl acid chloride)porphyrin iron(II) in methylene chloride, to yield a supported ultrathin polymeric membrane containing slightly more (i.e., 10 to 20%) porphyrin groups per unit weight than structure XIV in recurring units of the structure XV.



XV

Oxygen-transporting membranes can also be made from metallo-Schiff base compounds by the IP process. The incorporation of metallo-Schiff base complexes into an ultrathin membrane may be accomplished by the same general method described earlier. That is, two complementary derivatives of the metallo-Schiff base moiety are prepared, which are then reacted by IP.

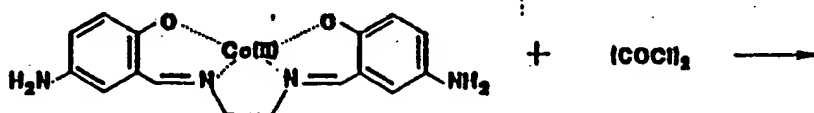
For example, the first derivative may have the general structure XVI



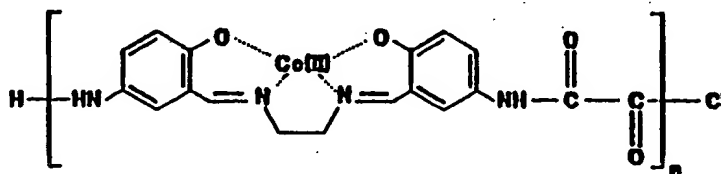
XVI

where at least two of the R groups are condensation-polymerizable functional groups (i.e., NH_2 , NHR , OH , NCO or COX where X is halide) or alkyl or aryl groups substituted with condensation-polymerizable functional groups, and the remaining R groups are selected from alkyl, aryl, alkoxy, aryloxy, nitro, halide, ketoxy, and amino. The second derivative may be essentially any compound that has two or more condensation-polymerizable functional groups that have complementary reactivity with the functional groups of the first derivative. Alternatively, one of the two reactants in the condensation reaction need not be a metallo-Schiff base. The polymer is formed as the polycondensation reaction product of the two reactants, the reaction taking place at the interface between two immiscible solvents, one containing the first reactant and the other containing the second reactant, on one surface of a microporous support. The poly-Schiff base can subsequently be converted to a polymetallo-Schiff base by contacting the polymer with a metal salt in the presence of a base.

An example of the formation of a polymetallo-Schiff base is the IP reaction, on the surface of a microporous support, of the diamine-functionalized cobalt-Schiff base XVII with a diacid chloride to form the polymeric Schiff base XVIII, as shown below:

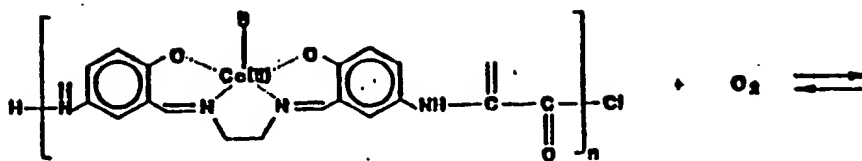


XVII

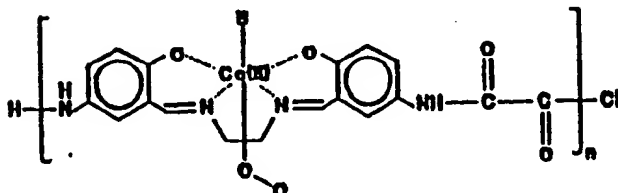


XVIII

Oxygen is reversibly bound by the polymeric Schiff base in the presence of an axial base, B, to form the adducts XIX and XIXa, according to the reaction:



XIX



XIXa

where B is an axial base selected from imidazoles, ketones, amides, amines, sulfoxides, pyridines and Lewis bases containing secondary or tertiary nitrogens. Preferred examples of axial bases include 1-methylimidazole, 2-methylimidazole, 1,2-dimethylimidazole, dimethylsulfoxide, N,N'-diethylenediamine, 4-dimethylaminopyridine, 4-aminopyridine, pyridine, 4-methylpyridine, 4-methylaminopyridine, 3,4-lutidine, 3,5-lutidine, 4-cyanopyridine, 4-methoxypyridine, 4,4-bipyridine, pyrazine, 4-pyrrolidinopyridine and N-methylpyrazinium halides.

Other moieties that can reversibly bind oxygen and can be incorporated into polymeric thin films according to the present invention include metallo-phthalocyanines and other transition metal complexes with four electron-donor atoms.

The oxygen-sorbing membranes described above may be used to extract oxygen from air as follows. One side of the membrane, the feed stream side, is placed in contact with air at atmospheric pressure. The other side of the membrane, the product stream side, is evacuated by means of a vacuum pump. The pressure differential this produces provides a driving force for gas permeation across the membrane. Because the membrane is much more permeable to oxygen than to nitrogen, the gas permeating the membrane will be enriched in oxygen. The process may also be carried out by pressurizing the feed stream and removing the oxygen-enriched air in the product stream at some lower pressure.

All of the oxygen-selective materials described above could also be used as selective sorbents. In use, the IP films would be exposed to a mixture of oxygen and other gases, such as air, at a pressure greater than atmospheric pressure. The oxygen would be selectively sorbed by the thin film. The pressure would then be reduced to atmospheric or less than atmospheric and the oxygen would be stripped off of the sorbent film.

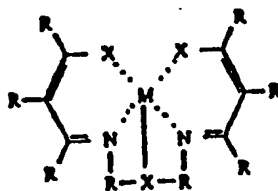
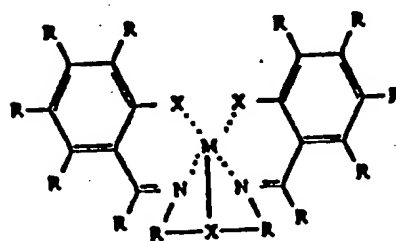
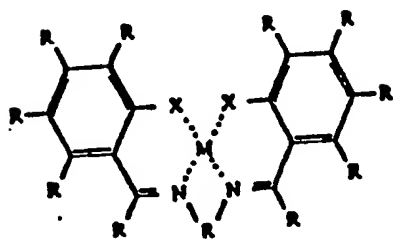
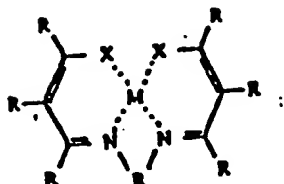
Claims

1. A composition of matter comprising the thin film interfacial polymerization reaction product of $M_F X_m$ and either $M_F Y_n$ or $N Y_n$ wherein M_F is a moiety having oxygen-specific reversibly-complexing complexing sites, N is a moiety not having any oxygen-specific complexing sites, X and Y are groups that are mutually reactive in a condensation reaction, and m and n are integers ≥ 2 .

2. The composition of matter of claim 1 wherein X and Y are selected from acid halides, amines, aldehydes, alcohols, thiols, isocyanates and sulfonyl halides.

3. The composition of matter of claim 1 wherein M_F is selected from metalloporphyrins, metallo-Schiff bases, and metallophthalocyanines.

4. The composition of matter of claim 3 wherein said metallo-Schiff base is selected from the structures



wherein M is a metal of +2 valence selected from cobalt, iron, copper, nickel, manganese, ruthenium and rhodium; X is -O-, -S-, -P- or -N-;

and R is hydrogen, alkyl, alkylene, aryl, arylene, halogen, alkoxy or a nitrogen-containing moiety.

5. The composition of matter of claim 3 wherein the metal of said metalloporphyrin, said metallo-Schiff base and said metallophthalocyanine is selected from cobalt(II) and iron(II).

6. The composition of matter of claim 5 comprising the interfacial polymerization reaction product of tetra-(aminophenyl)-porphyrin iron(II) and a polyacyl halide.

7. The composition of matter of claim 5 comprising the interfacial polymerization reaction product of tetra-(aminophenyl)-porphyrin cobalt(II) and a polyacyl halide.

8. The composition of matter of claim 6 or 7 wherein the polyacyl halide is selected from fumaryl chloride, tetra-(carboxyphenyl acid chloride)-porphyrin iron(II), and tetra-(carboxyphenyl acid chloride)-porphyrin cobalt(II).

9. A composite selective membrane comprising a microporous support and the thin film interfacial polymerization reaction product of any of claims 1-8.



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(54) Oxygen-complexing ultrathin films by interfacial polymerization.

(57) Interfacially-polymerized ultrathin films containing oxygen-complexing functional groups are disclosed, both with and without supports. Various applications are disclosed, including selective membranes and sorbents.

EP 0 369 713 A3



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 89 31 1730

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	PATENT ABSTRACTS OF JAPAN, vol. 11, no. 365 (C-460)[2812], 27th November 1987; & JP-A-62 136 226 (AGENCY OF IND. SCIENCE & TECHNOL.) 19-06-1987 ---		B 01 D 69/12 B 01 D 71/82 B 01 D 71/56 C 08 J 5/18 C 08 L 101/02 C 08 G 69/42 //
A	US-A-4 627 859 (J.J. ZUPANCIC) ---		C 01 B 13/02
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P,A	EP-A-0 304 818 (THE AGENCY OF INDUSTRIAL SCIENCE AND TECHNOLOGY) -----		
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			B 01 D 69/00 B 01 D 71/00
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 02-07-1990	Examiner DEVISME F.R.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure D : non-written document			
T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document			